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(21) International Application Number: PCT/US91/02242 (22) International Filing Date: 3 April 1991 (03.04.91) (30) Priority data: 509,122 16 April 1990 (16.04.90) US (71) Applicant: EASTMAN KODAK COMPANY [US/US]; 343 State Street, Rochester, NY 14650-2201 (US). (72) Inventors: SUMMER, Charles, Edwan, Jr. ; 4613 Wood- cliff Drive, Kingsport, TN 37664 (US). HITCH, Brenda, Jo ; 530 Windsor Forest Drive, Kingsport, TN 37663 (US). BERNARD, Bobby, Lynn ; Rt. 6, Box 208, Ro- gersville, TN 37857 (US).		(74) Agent: MARTIN, Charles, R.; 343 State Street, Rochester, NY 14650-2201 (US). (81) Designated States: AT (European patent), BE (European patent), CA, CH (European patent), DE (European pa- tent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), GR (Euro- pean patent), IT (European patent), JP, KR, LU (Euro- pean patent), NL (European patent), SE (European pa- tent). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the</i> <i>claims and to be republished in the event of the receipt of</i> <i>amendments.</i>
(54) Title: PROCESS FOR PREPARATION OF RESORCINOL BIS(DIHYDROXYETHYL)ETHER (57) Abstract A process for preparation of resorcinol bis(hydroxyethyl)ether by first contacting resorcinol with ethylene carbonate in the presence of water and an alkali metal carbonate and then adding a solution of water and an alkali metal hydroxide and then recovering the resorcinol bis(hydroxyethyl)ether by crystallization.		

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PROCESS FOR PREPARATION OF RESORCINOL BIS(DIHYDROXYETHYL) ETHER

This invention relates to a process for preparation of resorcinol bis(hydroxyethyl)ether by first contacting resorcinol with ethylene carbonate in the presence of water and an alkali metal carbonate and then adding a solution of water and an alkali metal hydroxide and then recovering the resorcinol bis(hydroxyethyl)ether by crystallization.

As disclosed in U.S. 2,766,292 phenols are known to react with ethylene carbonate in the presence of an alkali carbonate catalyst to produce the corresponding hydroxyethyl ether. When this procedure is applied to dihydroxybenzenes preparation of the bis(2-hydroxyethyl)ether is accompanied by several by-products including hydroxyethoxyphenols, (2-hydroxyethyl)oxyethyl phenyl ethers, and polymeric materials which manifests themselves as an oil in the product. These by-products render the bis(2-hydroxyethyl)ether compounds unsuitable for many applications. Furthermore, the oil like polymer by-product inhibits the crystallization of the bis(2-hydroxyethyl)ether thus complicating its isolation and purification.

The process of this invention is an improvement over the prior art because in this process of this invention a higher yield and purity is obtained by conducting the additional step of adding a solution of water and sodium hydroxide to the reaction products of the reaction of resorcinol and ethylene carbonate prior to crystallization to recover the resorcinol bis(hydroxyethyl)ether.

The process of the invention is composed of three steps. The first step is contacting resorcinol and ethylene carbonate in the presence of water and an alkali metal carbonate. Then a solution of water and an

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alkali metal hydroxide which is at least 0.6 molar is added to the reaction products of the first step. Then the resorcinol bis(hydroxyethyl)ether is recovered by crystallization.

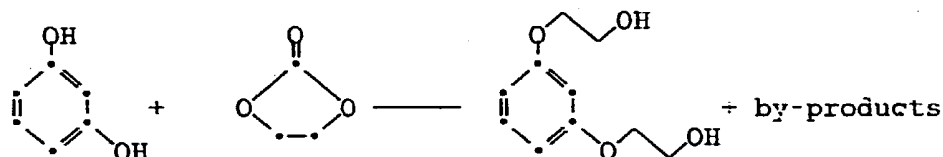
5 In the first step of the process resorcinol reacts with ethylene carbonate in the presence of water and an alkali metal carbonate to produce resorcinol bis(hydroxyethyl)ether and a variety of unwanted by-products according to the following reaction

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The reaction is conducted for a sufficient length of time and at a sufficient temperature for the resorcinol bis(hydroxyethyl)ether to form in good yield. A temperature in the range of 130°-150°C is particularly satisfactory. Typically the reaction time is 1 to 10 hours, preferably 4 to 6 hours.

35 The reaction can be conducted commercially in general purpose stirred reactors.

The alkali metal in this alkali metal carbonate can be any alkali metal but potassium is preferred.

In the second step of the process a solution of water and an alkali metal hydroxide is added to the reaction products of the first step composed of resorcinol bis(hydroxyethyl)ether and various unwanted by-products. The alkali metal in the alkali metal hydroxide can be lithium, sodium, or potassium but sodium is preferred. The solution is at least 0.6 molar, preferably at least 0.9 molar. The concentration of the caustic solution can be as low as

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2% and as high as 20%. A concentration of 3-8% is optimal, and 4% is preferred. The rate at which the solution is added is such that the temperature of the mixture is maintained at 50 to 90°C.

5 The second step can be conducted commercially by adding the caustic solution to the same standard stirred reactor used to conduct the first step.

 The third step of the process is recovery of the resorcinol bis(hydroxyethyl)ether by crystallization.
10 The resorcinol bis(hydroxyethyl)ether is recovered from the result of adding the solution of water and alkali metal hydroxide to the reaction products of the first step by conventional crystallization technique well known in the art. For example the crystallization can
15 be accomplished by simply cooling the mixture until the resorcinol bis(hydroxyethyl)ether precipitates, and recover the precipitate.

 The resorcinol bis(hydroxyethyl)ether prepared by the process of this invention is useful as a
20 polyurethane chain extender and as an intermediate for phenylenedioxydiacetic acid derivatives which are known to impart enhanced gas barrier properties to polyesters.

Example 1

 This example illustrates the prior art where there
25 is no solution of water and an alkali metal hydroxide added to the reaction products of step one prior to recovery by crystallization.

 To a 12L flask equipped with a stirrer, reflux condenser, N₂ inlet, addition funnel, and heating mantle
30 was added ethylene carbonate (1,936 g; 22 mole), resorcinol (1,101 g; 10 mole) and potassium carbonate (10 g; .07 mole). The apparatus was purged with N₂ until the oxygen content was measured to be less than

- 4 -

1%. The mixture was stirred and gradually heated to 140°C. When the temperature reached 40°C, the stirring speed was increased to 100 rpm. At 125°C, the mixture began to evolve CO₂. The mixture was heated at 140°C for 6 hours, after which time it was cooled to 90°C, and 4L of water was added at a rate of 44 mL/min. while the temperature was maintained above 50°C. The resulting mixture was stirred at 100 rpm and cooled to 50°C. Resorcinol bis(hydroxyethyl)ether (2 g) was added as seed crystals and the mixture was cooled to 18°C at a rate of 5°/min. and held at this temperature for 1 hour. The product was collected by filtration, washed twice with 1 L portions of water, and dried in a vacuum oven at 50°C. The yield was 1,366 g (69%) and contained an oily material which separated upon dissolving the material in warm water.

Example 2

This example illustrates practice of the invention.

To a 1 L 3-neck flask equipped with a mechanical stirrer, heating mantle, reflux condenser, thermocouple well, and argon atmosphere, was added resorcinol (110g; 1 mole), ethylene carbonate (194g; 2.2 mole), and potassium carbonate (1g; 7 mole). The resulting mixture was heated at 140°C for 6 hours during which time CO₂ was evolved. The mixture was cooled to 90°C and 400 mL of 4% NaOH solution was added over a 10 min. period while the temperature of the mixture was allowed to decrease to 53°C. The mixture was allowed to slowly cool to 20°C to precipitate the resorcinol bis(hydroxyethyl)ether, and the resorcinol bis(hydroxyethyl)ether was collected by filtration,

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washed with 50 mL of water, and dried for 12 hours in a vacuum oven. The dry product weighed 186g (94%).

Examples 3-7

The invention was practiced by repeating Example 1 except 4 L of a sodium hydroxide solution was used in place of the 4 L of water. The presence of an oil-like by-product and the yield of resorcinol bis(hydroxyethyl)ether as a function of the concentration of NaOH used in the solution is summarized below.

	<u>Example No.</u>	<u>NaOH</u>	<u>Yield</u>	<u>Oil-like By-product Present</u>
	3	0.25 M	80.7%	yes
15	4	0.38 M	83.3%	yes
	5	0.50 M	86.2%	yes
	6	0.63 M	93.0%	yes
	7	1.00 M	94.4%	no

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CLAIMS

1. A process for preparation of resorcinol
bis(hydroxyethyl)ether comprising
 - (A) contacting resorcinol and ethylene
5 carbonate in the presence of water and
an alkali metal carbonate,
 - (B) adding a solution of water and an alkali
metal hydroxide which is at least 0.5
molar, and
 - 10 (C) recovering the resorcinol
bis(hydroxyethyl)ether by
crystallization.
2. A process for preparation of resorcinol
bis(hydroxyethyl)ether comprising
 - 15 (A) contacting resorcinol and ethylene
carbonate in the presence of water and
potassium carbonate,
 - (B) adding a solution of water and sodium
hydroxide which is at least 0.9 molar,
and
 - 20 (C) recovering the resorcinol
bis(hydroxyethyl)ether by
crystallization.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 91/02242

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶ According to International Patent Classification (IPC) or to both National Classification and IPC IPC ⁵ : C 07 C 43/23, C 07 C 41/16													
II. FIELDS SEARCHED <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black;">Minimum Documentation Searched ⁷</div> <table style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 25%; border-bottom: 1px solid black;">Classification System</th> <th style="border-bottom: 1px solid black;">Classification Symbols</th> </tr> <tr> <td style="padding: 5px; vertical-align: top;">IPC⁵</td> <td style="padding: 5px; vertical-align: top;">C 07 C 41/00, C 07 C 43/00</td> </tr> </table> <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black;">Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸</div>			Classification System	Classification Symbols	IPC ⁵	C 07 C 41/00, C 07 C 43/00							
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III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹ <table style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 10%; border-bottom: 1px solid black;">Category ⁹</th> <th style="border-bottom: 1px solid black;">Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²</th> <th style="width: 10%; border-bottom: 1px solid black;">Relevant to Claim No. ¹³</th> </tr> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">A</td> <td style="padding: 5px;"> Journal of The American Chemical Society, volume 79, no. 3, 12 February 1957, American Chemical Society, E. Dyer et al.: "The preparation of polymeric and cyclic urethans and ureas from ethylene carbonate and amines", pages 672-675 see page 674, example A <div style="text-align: center;">--</div> </td> <td style="text-align: center; vertical-align: top; padding: 5px;">1-2</td> </tr> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">A</td> <td style="padding: 5px;"> Tetrahedron Letters, volume 29, no. 2, 1988, Pergamon Journals Ltd., (GB), M.C. Pirrung et al.: "Photochemical rearrangements of quinone monoketals. Synthesis of substituted cyclopente- nones", pages 163-166 see page 164, line 2; scheme 2 <div style="text-align: center;">--</div> <div style="text-align: right;">./.</div> </td> <td style="text-align: center; vertical-align: top; padding: 5px;">1-2</td> </tr> </table> <div style="font-size: small; padding: 5px;"> <table style="width: 100%;"> <tr> <td style="vertical-align: top; width: 50%;"> ¹⁰ Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed </td> <td style="vertical-align: top; width: 50%;"> "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "Z" document member of the same patent family </td> </tr> </table> </div>			Category ⁹	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³	A	Journal of The American Chemical Society, volume 79, no. 3, 12 February 1957, American Chemical Society, E. Dyer et al.: "The preparation of polymeric and cyclic urethans and ureas from ethylene carbonate and amines", pages 672-675 see page 674, example A <div style="text-align: center;">--</div>	1-2	A	Tetrahedron Letters, volume 29, no. 2, 1988, Pergamon Journals Ltd., (GB), M.C. Pirrung et al.: "Photochemical rearrangements of quinone monoketals. Synthesis of substituted cyclopente- nones", pages 163-166 see page 164, line 2; scheme 2 <div style="text-align: center;">--</div> <div style="text-align: right;">./.</div>	1-2	¹⁰ Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "Z" document member of the same patent family
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IV. CERTIFICATION <table style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 50%; padding: 5px; vertical-align: top;"> Date of the Actual Completion of the International Search <div style="text-align: center;">20th June 1991</div> </td> <td style="width: 50%; padding: 5px; vertical-align: top;"> Date of Mailing of this International Search Report <div style="text-align: center;">29.08.91</div> </td> </tr> <tr> <td style="padding: 5px; vertical-align: top;"> International Searching Authority <div style="text-align: center;">EUROPEAN PATENT OFFICE</div> </td> <td style="padding: 5px; vertical-align: top;"> Signature of Authorized Officer <div style="text-align: center;">F.W. HECK</div> <div style="text-align: right; font-family: cursive; font-size: 1.5em;">Heck</div> </td> </tr> </table>			Date of the Actual Completion of the International Search <div style="text-align: center;">20th June 1991</div>	Date of Mailing of this International Search Report <div style="text-align: center;">29.08.91</div>	International Searching Authority <div style="text-align: center;">EUROPEAN PATENT OFFICE</div>	Signature of Authorized Officer <div style="text-align: center;">F.W. HECK</div> <div style="text-align: right; font-family: cursive; font-size: 1.5em;">Heck</div>							
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III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, " with indication, where appropriate, of the relevant passages	Relevant to Claim No.
P,A	Patent Abstracts of Japan, volume 14, no. 294 (C-732)(4237), 26 June 1990 & JP, A, 296545 (TAOKA CHEM. CO. LTD), 9 April 1990 see the whole abstract --	1-2
A	Chemical Abstracts, volume 90, no. 23, 4 June 1979, American Chemical Society, (Columbus, Ohio, US), see page 627, abstract no. 186567b & JP, A, 7901291 (MITSUBISHI PETRO- CHEMICAL CO., LTD), 23 January 1979 -----	1-2